Institute for Climate and Atmospheric Science
School of Earth and Environment
FACULTY OF ENVIRONMENT

UNIVERSITY OF LEEDS

Air quality monitoring: Techniques and instrumentation

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On average you breathe 12000 - 15000 litres of air every day… at ~1.29 g/L that is in excess of 15 kg, that is several times more than you consume as food/drink.

What do you know already?????

Air Pollution – Many (many) sources….



















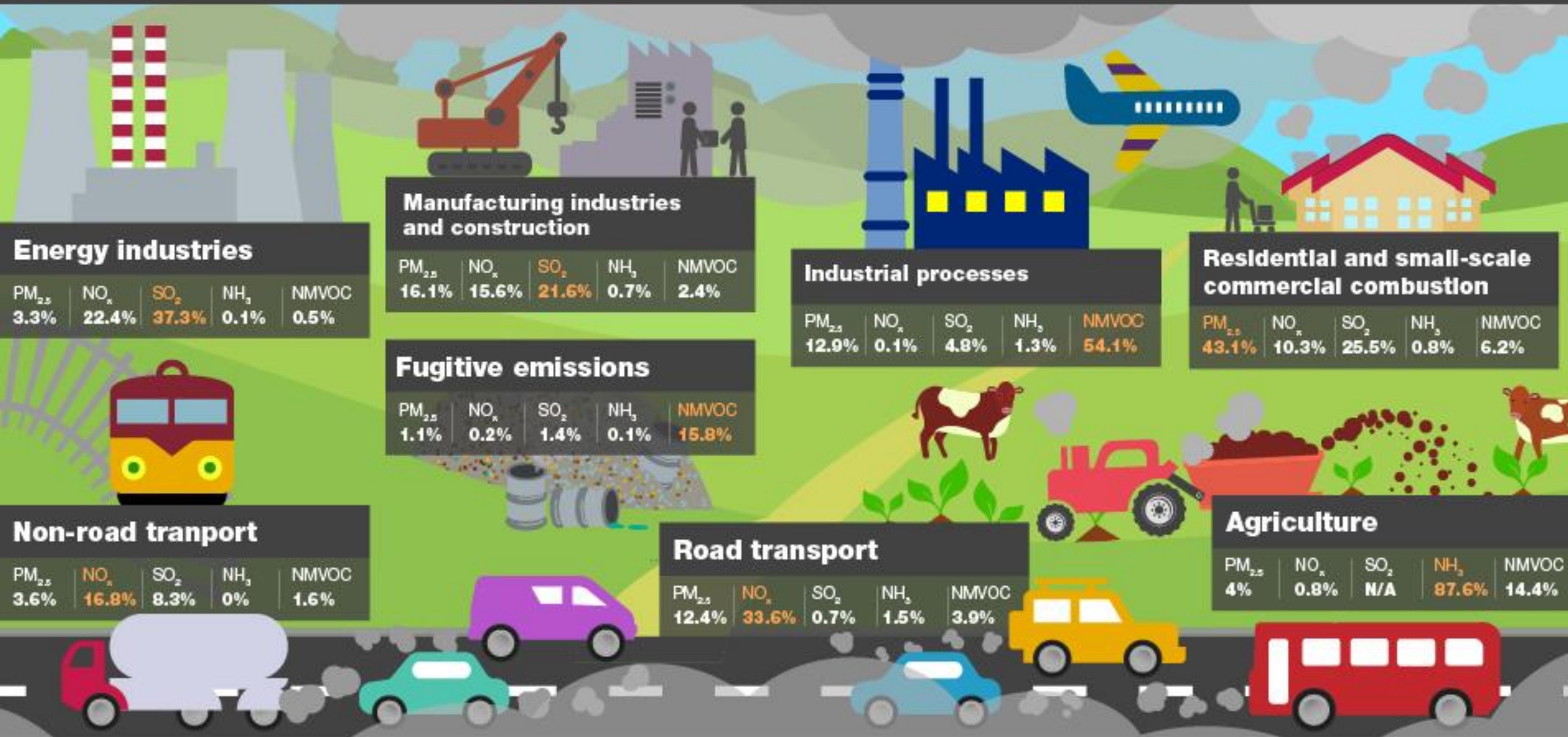


Extra Challenges….

Public Health England

Health Matters

Sources of air pollution



Pollution substances:

- **SO_2** - Sulphur dioxide
- **NO_x** - Nitrogen oxides
- **NH_3** - Ammonia
- **$PM_{2.5}$** - Primary particulate matter
- **NMVOCs** - Non-methane volatile organic compounds

Air Pollution => Health

Needs many disciplines to understand

Making measurements matter!

Many **analytical techniques** and instruments are used for environmental measurement.

An APPROPRIATE method must be chosen for each analysis

When deciding how samples will be collected, there are other considerations apart from where the samples will be taken:

When to take samples, how many samples are required.

- How to take samples.
- How the samples must be treated prior to analysis.
- How to store and preserve samples up to the point of analysis.

SAMPLING STRATEGY

- What are the objectives of the study?.
- What is the 'type' of system that is going to be observed?.
- What resources are required/available for the study?.
- Will the samples give a **fair representation** of the environment studied?.

The key is to produce something which is

REPRESENTATIVE

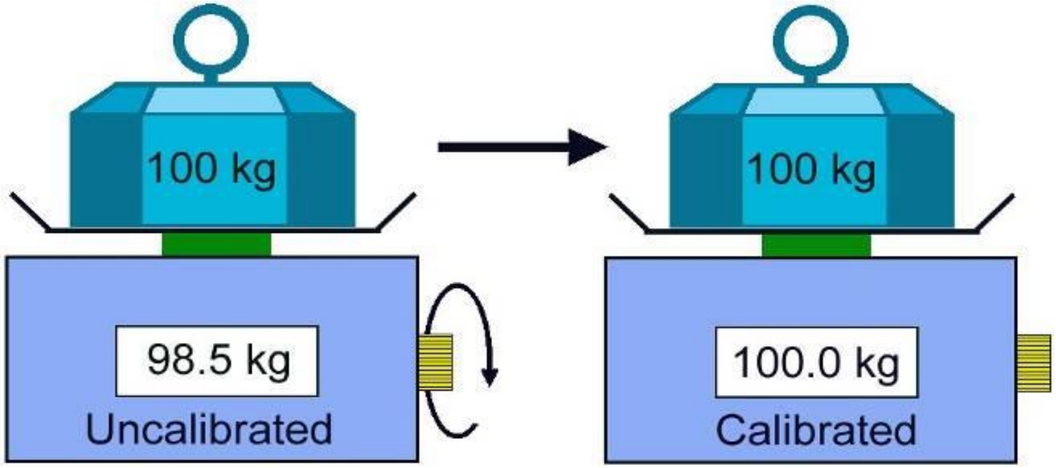
Are your measurements in the right place?

Are they fast enough?

Long enough dataset?

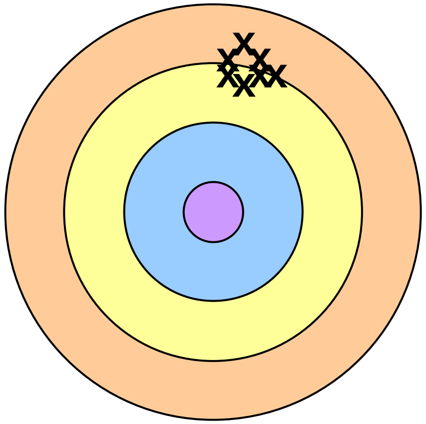
How GOOD are they?

Calibration and standards

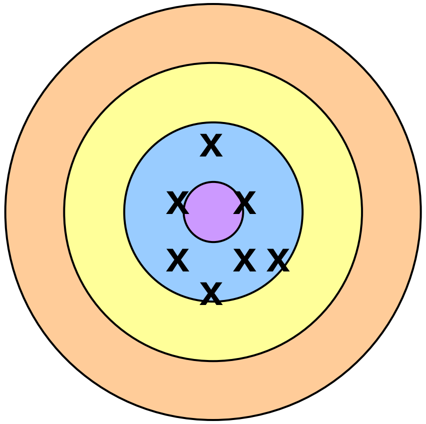


Precision and accuracy – The Dartboard Model

The uncertainty which errors give to a final result is described as its ‘precision’.



The ‘accuracy’ of a result is the difference between the experimental result and the ‘known’ value.



Monitoring Air Quality

Which atmospheric constituents are pollutants?

Ozone

Mercury

NO_2

CO

SO_2

Lead

Particulates

Organics

Constituents important for air quality and climate are ‘trace’ gases - present in **<u>very</u>** small concentrations (parts per billion or parts per trillion).

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- Mercury
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- CO
- SO_2
- Lead
- Particulates
- Organics

Constituents important for air quality and climate are ‘trace’ gases - present in very small concentrations (parts per billion or parts per trillion).

Which atmospheric constituents are pollutants?

Ozone

- Found in abundance in stratosphere.
- Harmful at ground level.
- Formed by chemistry in the air under sunlight.

NO_2

- Emitted in high temperature combustion.
- Road traffic biggest UK source.
- UK currently breaking EU law for NO_2 levels.

Particulates

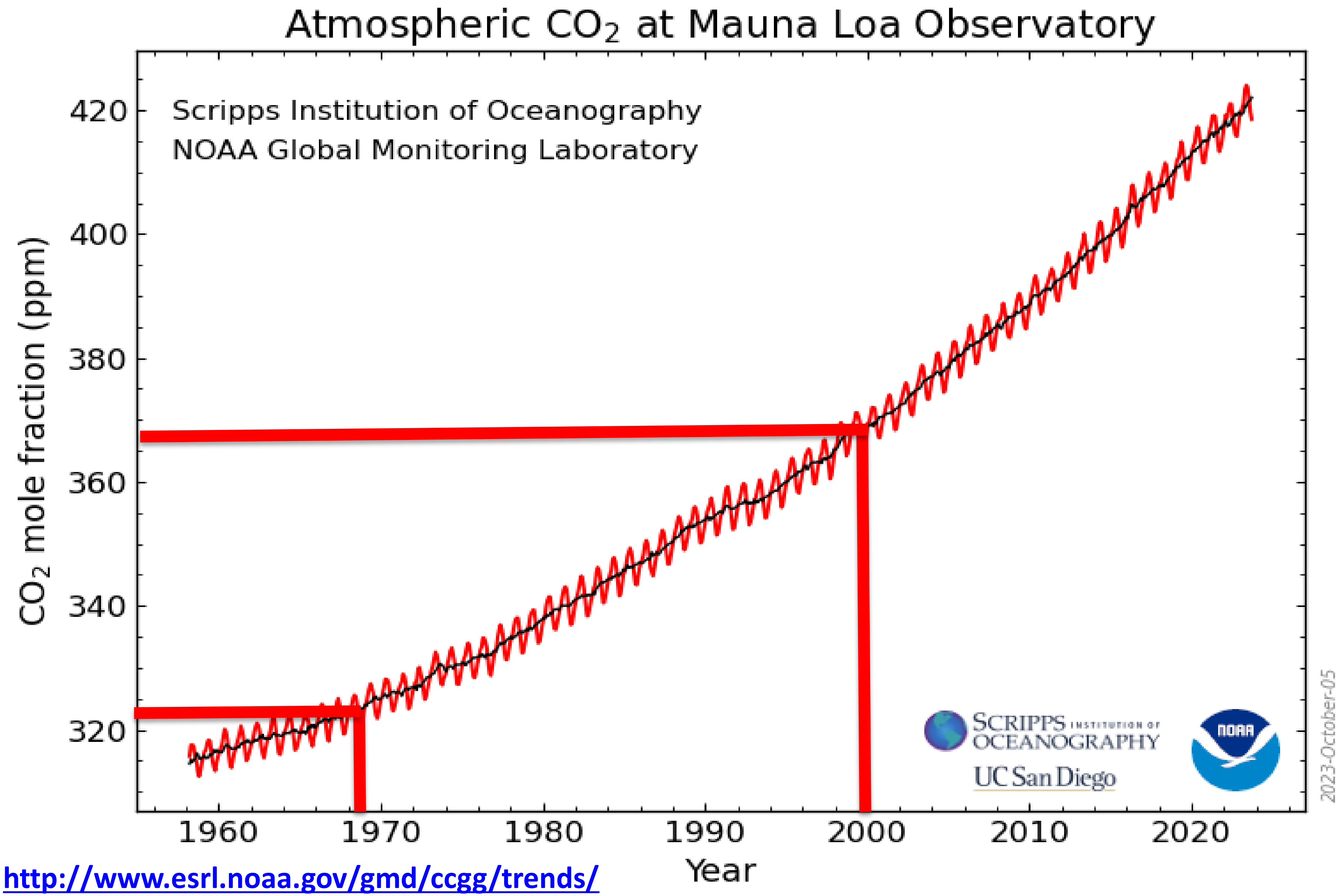
- Tiny particles suspended in air.
- Can be smaller than width of human hair.
- Emitted directly but can also form in atmosphere.

SO_2

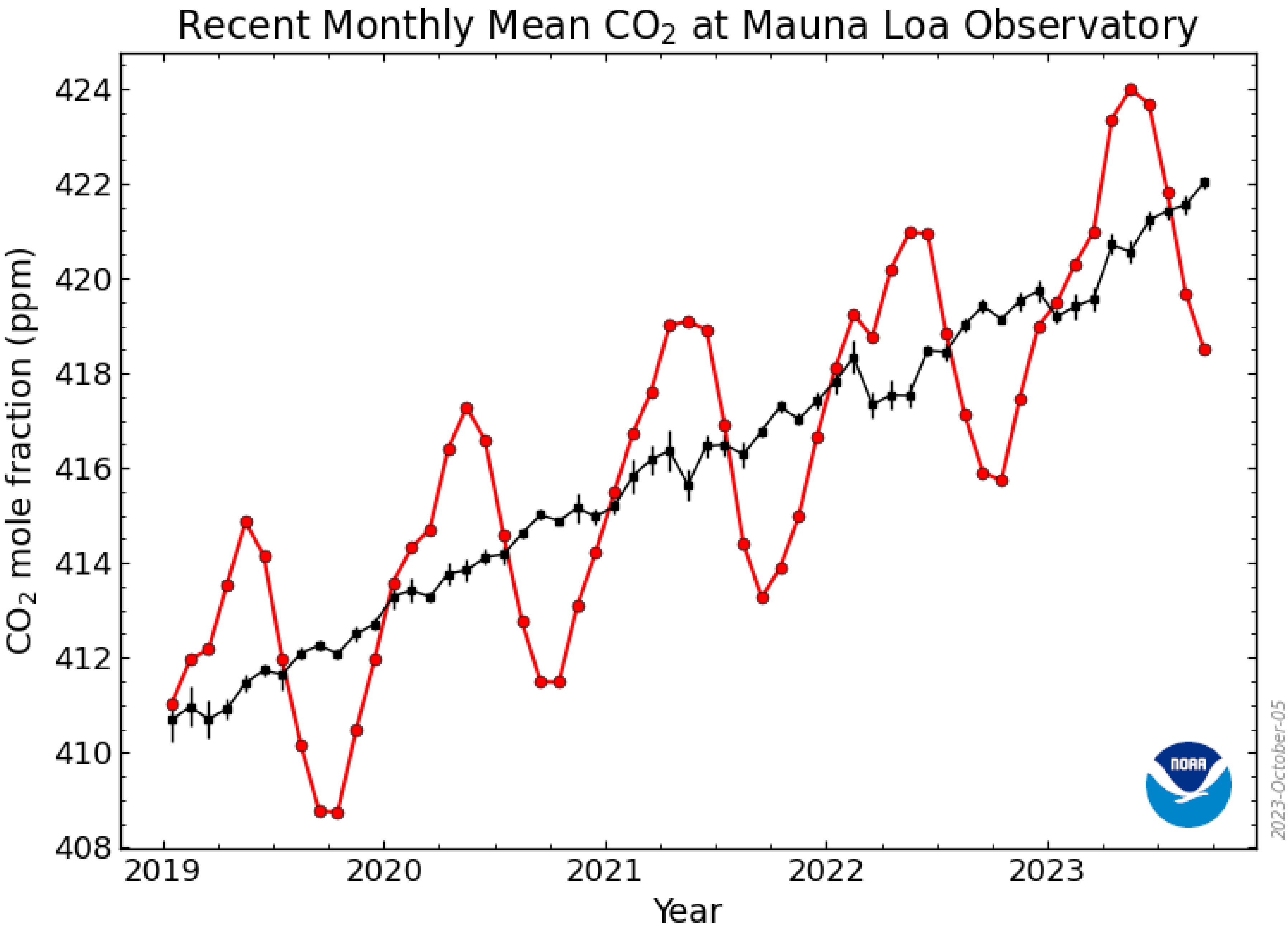
- Sourced from coal and fossil fuels.
- Reacts in atmosphere to form particles (sulfates).
- Can lead to 'acid rain'.

Most “famous” Environmental Measurement?

Most "famous" Environmental Measurement?

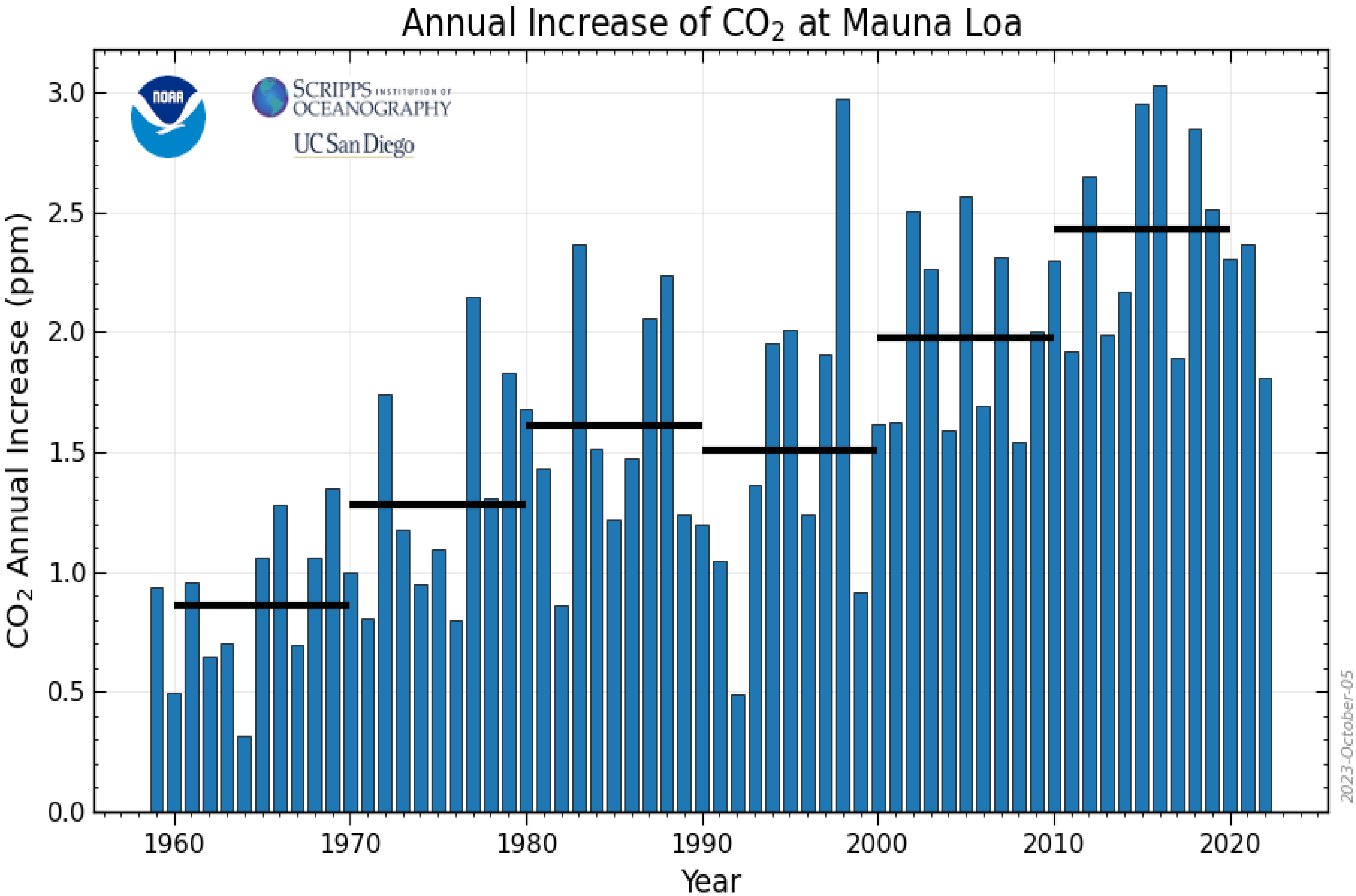


http://www.esrl.noaa.gov/gmd/ccgg/trends/



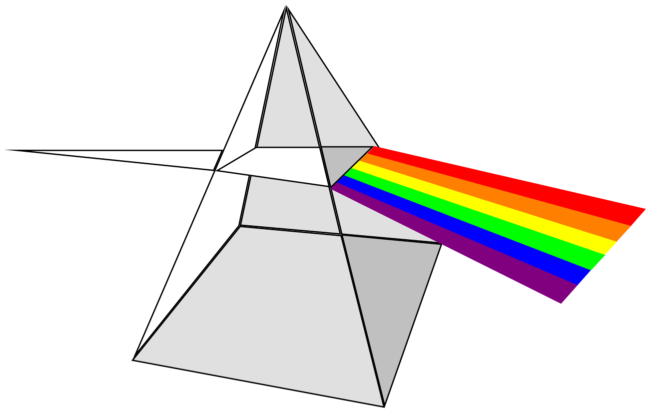
http://www.esrl.noaa.gov/gmd/ccgg/trends/

It's much more than just raw numbers though!



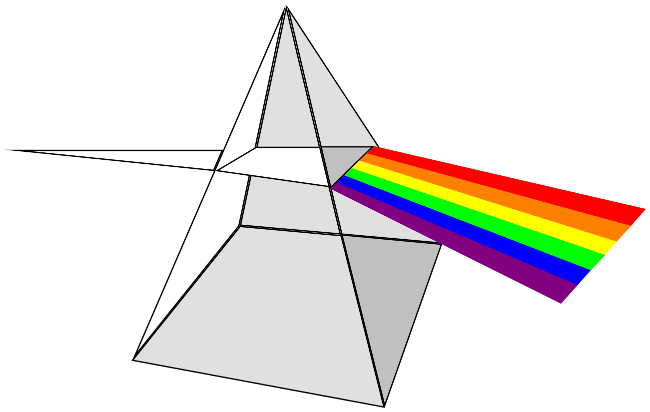
https://gml.noaa.gov/ccgg/trends/gr.html

Spectroscopic methods



Spectroscopy is the use of the absorption, emission, or scattering of electromagnetic radiation by matter to qualitatively or quantitatively study atoms, molecules, atomic or molecular ions, or solids.

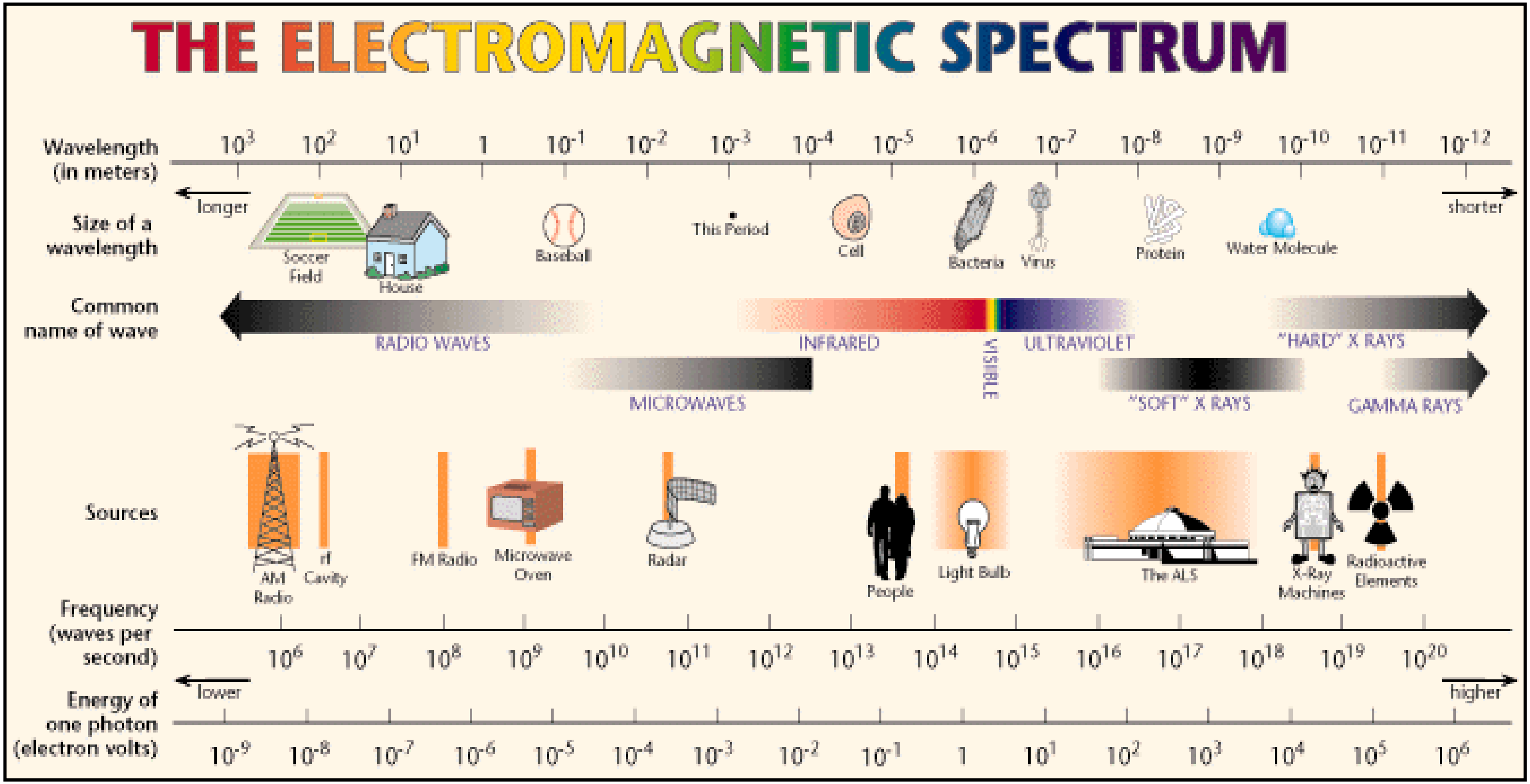
- **The energy can be absorbed; the transfer of energy from the radiation to an absorber, atom, molecule, or solid.**



- **Energy can be emitted; from a species previously excited by photon absorption.**

In all cases it is stored in discrete quantities or *quantised* levels e.g. to adsorb energy from a photon, the photon must have exactly the same energy of the transition between energy levels

- **The light can be scattered; a redirection of the photon which is sometimes accompanied by a change in energy.**



Light photons of different energies classified into different spectral regions.

These regions have the same electromagnetic nature, but because of their very different energies they interact with matter very differently.

Spectroscopic instrumentation

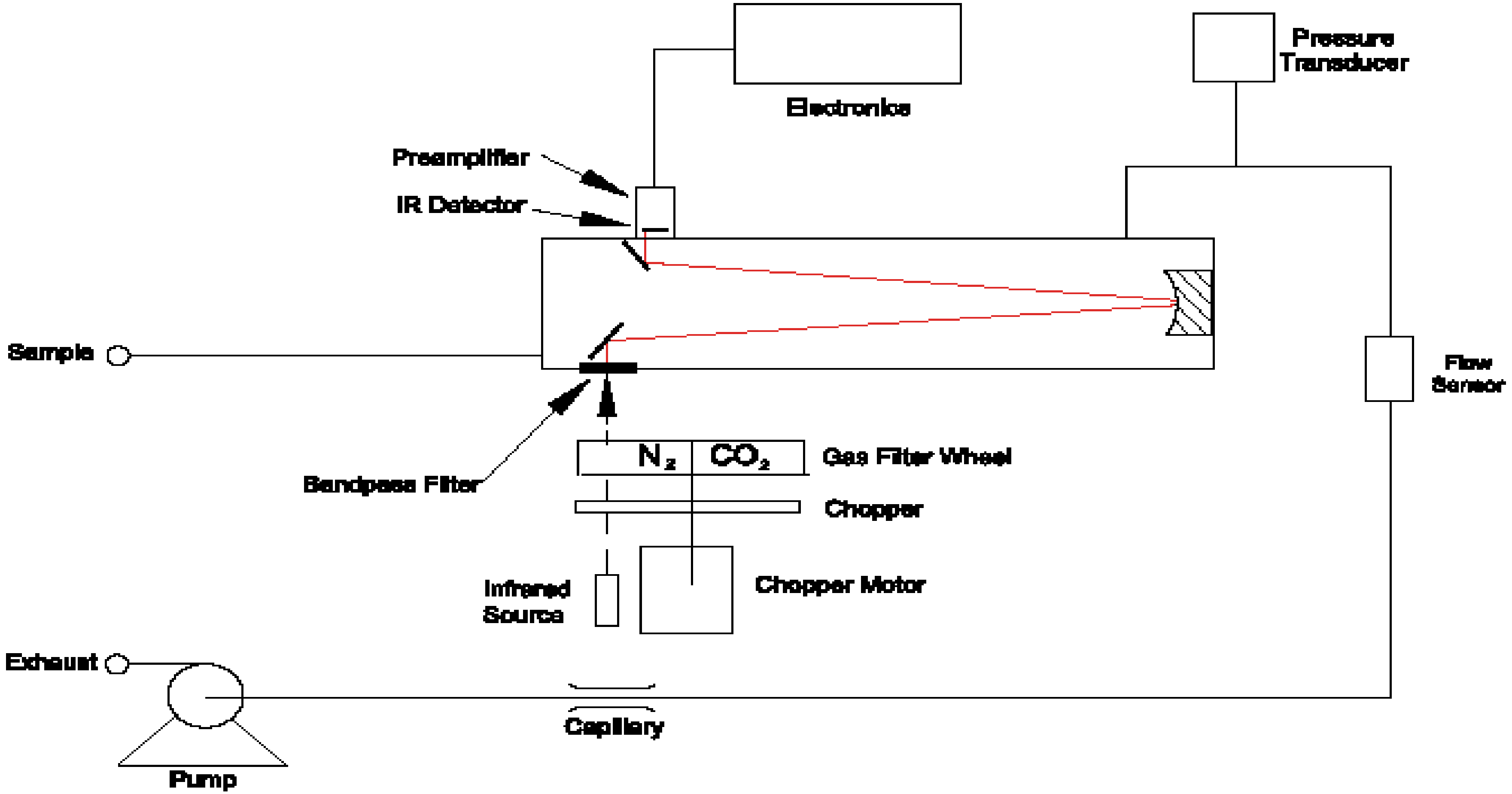
Three parts to a spectroscopic instrument.

- **Light sources**
- **Monochromators**
- **Detectors**

There are many variations and hybrids of spectroscopic techniques, but all follow the same basic theories.

The general layout of energy source, energy absorption and energy detection is consistent throughout.

Carbon Dioxide (CO_2) by IR.



The filter modulates the light produced and the difference between the light detected on the photomultiplier is proportional to the gas concentration in the cell.

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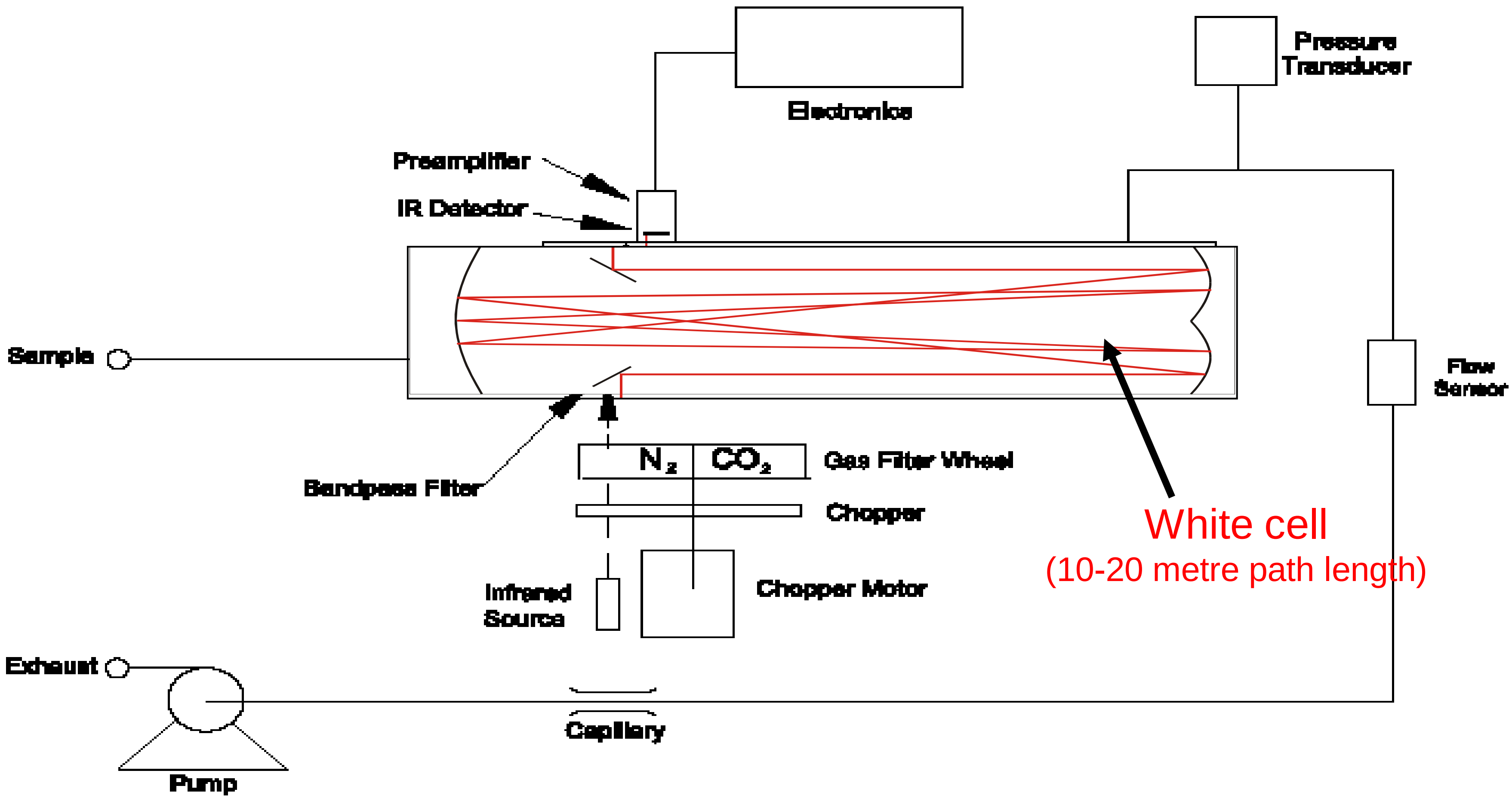


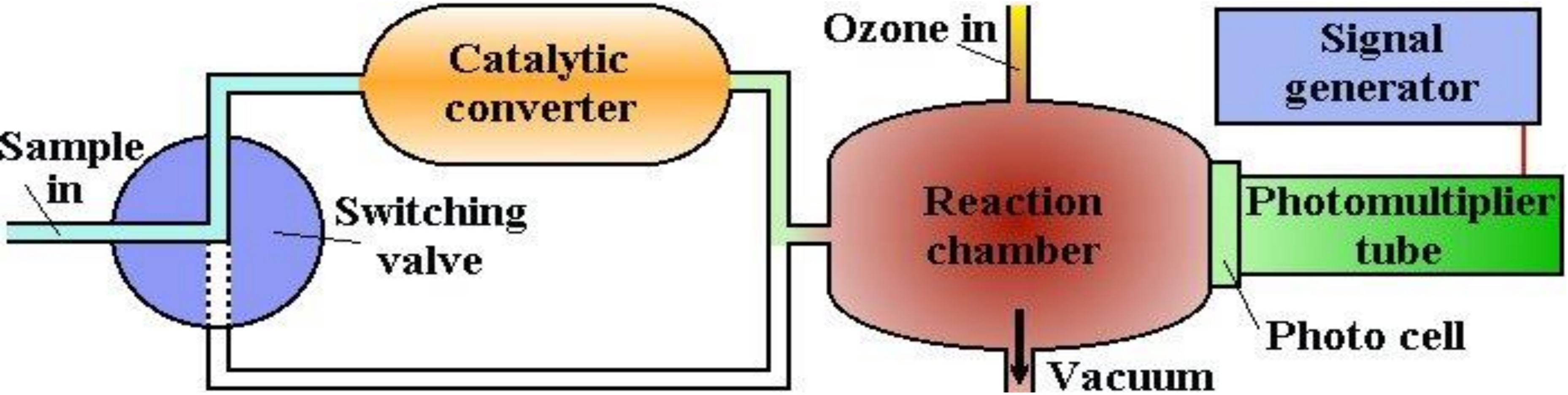
The filter modulates the light produced and the difference between the light detected on the photomultiplier is proportional to the gas concentration in the cell.

NOx by Chemiluminescence.

$NO + O_3 \rightarrow NO_2^* + O_2$ subsequently $NO_2^* \rightarrow NO_2 + h\upsilon$

The NO_2^* species is simply NO_2 in an excited (electronic) state which in time relaxes to emit photons of light. The radiation has a range of wavelengths but is strongest centered around 1200 nm in the near infrared region.

The light intensity varies linearly as predicted by the Beer-Lambert relationship which can be expressed in the form: $\ln(I_T/I_0) = -\varepsilon cl$



The technique ONLY measures NO so it converts NO_2 into NO by reducing it over a hot metal surface: $3NO_2 + Mo \rightarrow 3NO + MoO_3$ (315°C)

Switching between convertor and direct gives [NOx] and [NO] (NO_2 by subtraction.)

Ozone (O_3).

Ozone is relatively abundant in the troposphere (0 - 400 ppbV)

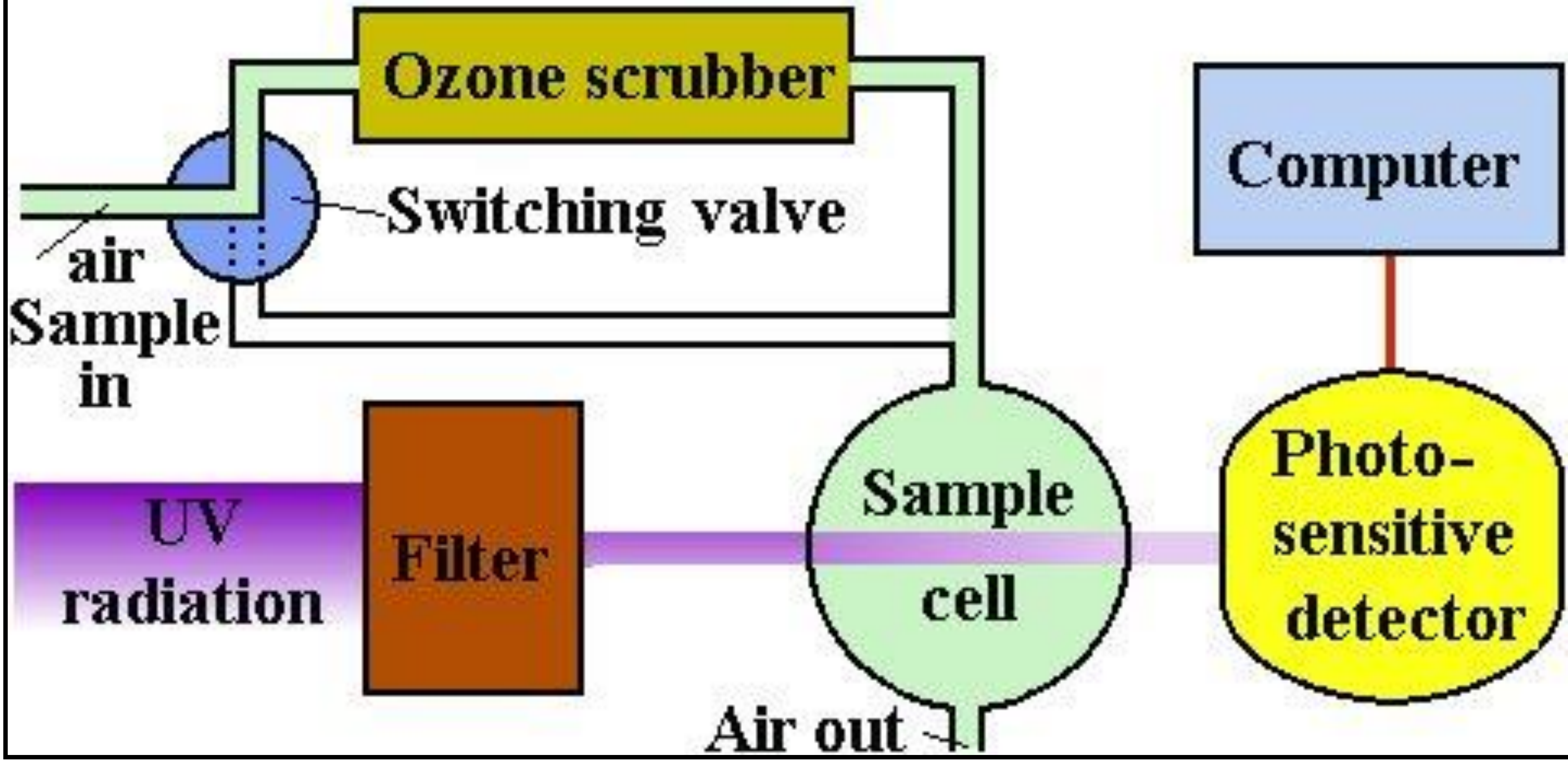
There are no specific wet chemical methods for the analysis of ozone, although a broad oxidant method using the oxidation of potassium iodide is available (interferences from alkyl nitrates, hydrogen peroxide and even, to a limited extent nitrogen dioxide).

It is the strong absorption of ozone in the 254 nm region in the stratosphere that protects life lower in the atmosphere.

First reported use of absorption spectroscopy was in 1912, modern instruments generally use ultraviolet photometry at 253.7 nm for direct determination of atmospheric ozone.

Light is produced by a mercury vapour lamp, the majority of the light emitted is at the 254 nm wavelength, it is this wavelength that there is a strong absorption.

Some hydrocarbons particularly aromatics can also absorb BUT only when present in high concentrations (chemical plants, biomass burning plumes).



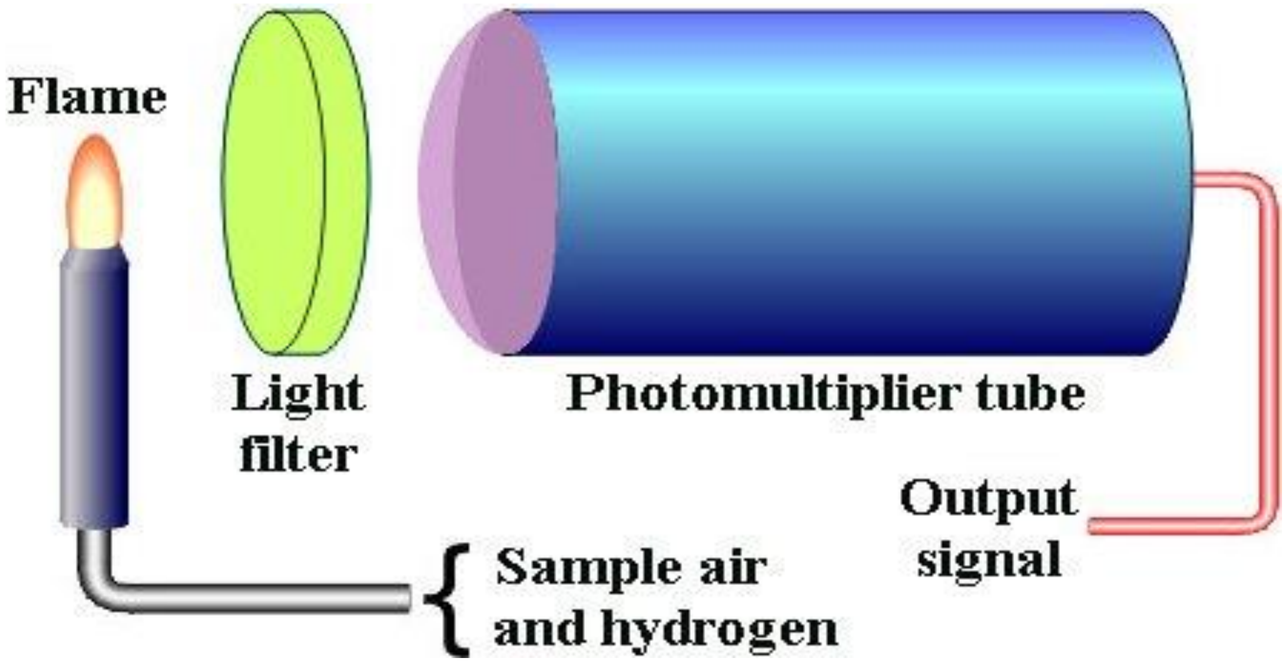
Continuous flow of air passes into sample cell where it is exposed to UV @ 254 nm.

Ozone absorbs a portion of photons, remainder detected by a photodetector.

An in-line ozone scrubber produces a zero measurement, the difference in absorption is determined and thus a value for the concentration of ozone. (BEER LAMBERT)

Sulphur Dioxide (SO_2).

To detect SO_2 a flame photometric detector (FPD) can be used.



The FPD is used to continuously measure sulphur compounds in ambient air.

Light is emitted in the near UV region when the sulphur compounds are thermally decomposed in a hydrogen flame.

This technique can be applied to GC if the air contains a number of sulphur containing compounds such as H_2S.

Particulate Matter

THE RELATIVE SIZE **OF PARTICLES**

From the COVID-19 pandemic to the U.S. West Coast wildfires, some of the biggest threats now are also the most microscopic.

A particle needs to be 10 microns (μm) or less before it can be inhaled into your respiratory tract. But just how small are these specks?

Here's a look at the relative sizes of some familiar particles ↘

SOURCES Clearstream, Daniel Loverboy, EPA, Financial Times, News Medical, Science Direct, SCMP, Susan Sokolowski, Petroclear, U.S. Dept. of Energy

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VISUAL CAPITALIST

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PENETRATION OF PARTICLES INTO THE BODY

PM10	PM2.5 & PM1	PM0.1
COARSE PARTICLES	FINE PARTICLES	ULTRAFINE PARTICLES
Pollen Wood burning Dust Construction Fireworks Road traffic	Wood burning Car exhaust Biomass Agricultural burning Fireworks Cooking Bacteria & Fungi	Wood burning Car exhaust Biomass Agricultural burning Viruses

#SEETHEAIR

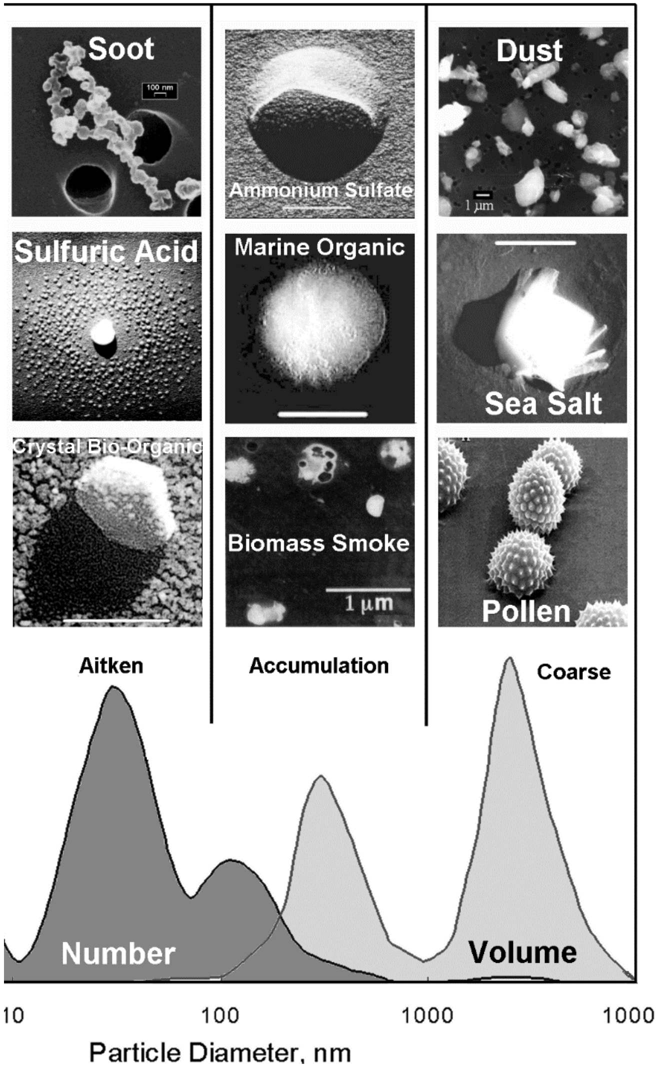
How much: Mass Loading

Filter Sampling - Simple, low resolution.

Cascade Sampling - More size fractions, still low resolution

TEOM - Single size range BUT much high temporal resolution

Example of a In Situ Measurement: Filter Sampling



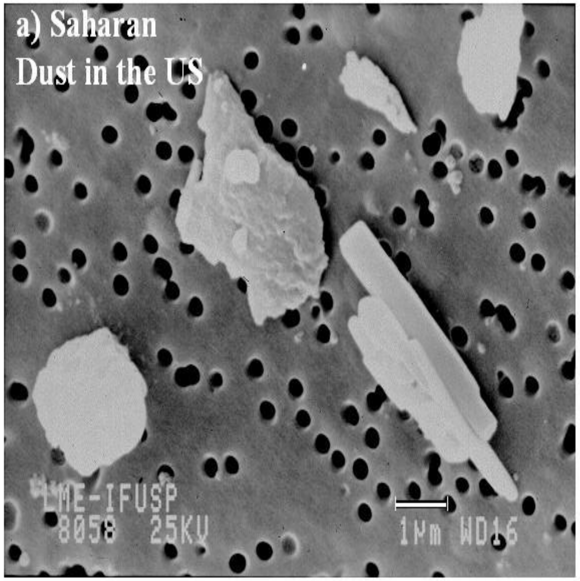
The pore size of the filter can be used to add a degree of selectivity in particle size collected.

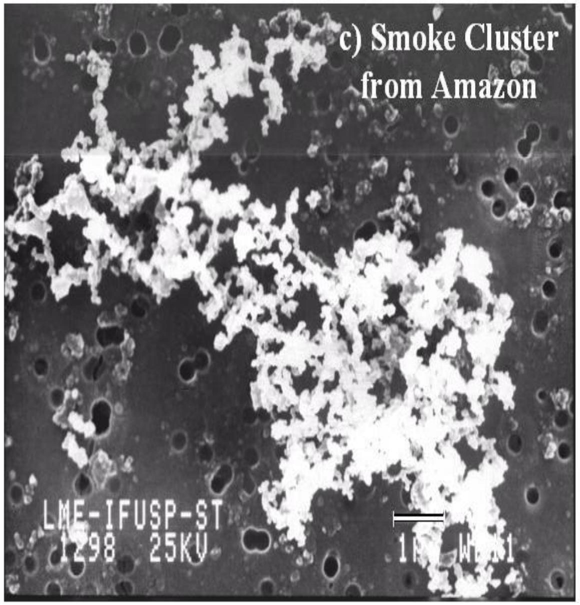
V. large sample volumes are required, typically 50-1500 m^3

Total flow rate required for calculation of concentration.

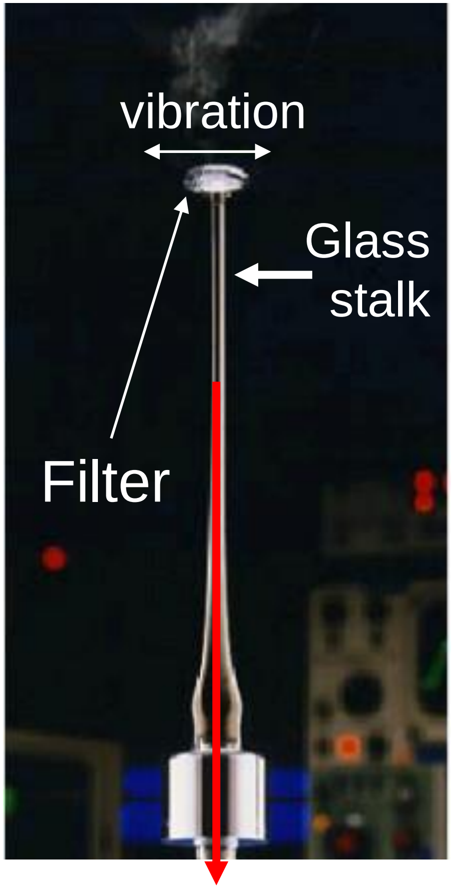
Filters must be measured before exposure and kept cool once they have been used when analysing for VOC.

Comprehensive analysis may use extraction followed by LC or GC + MS also electron microscopy or ice nucleation detection methods





TEOM - Taped Element Oscillating Microbalance.



Air drawn down central tube by calibrated pump

•A filter is mounted on the top of a glass stalk which vibrates horizontally at high frequency (200-600 Hz).

•The sample flow passes through the filter, where particulate matter collects, and then continues through the hollow tapered element on its way to an active volumetric flow control system and vacuum pump.

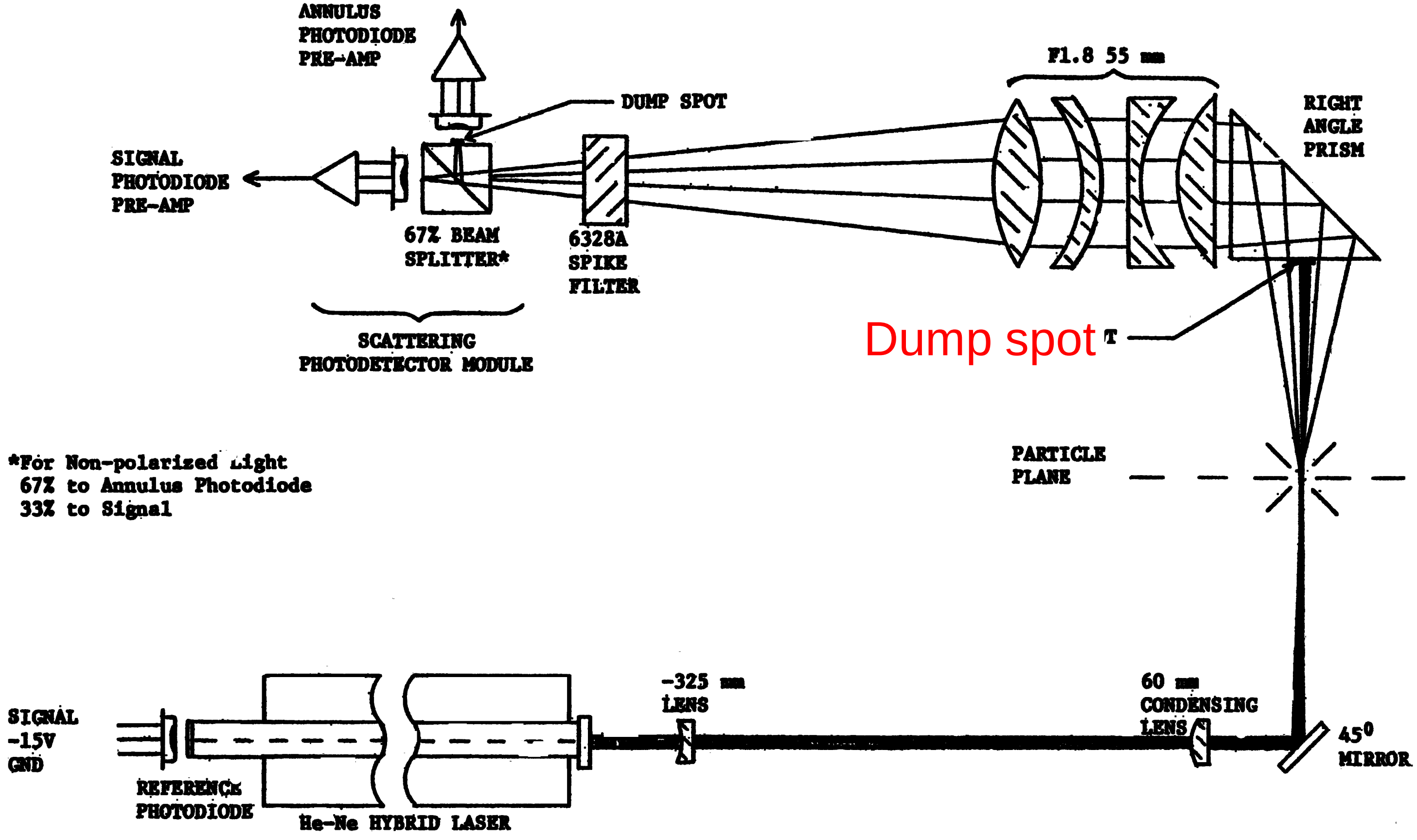
•As particulate material is deposited on the filter the resonant frequency of the element changes.

•An inertial balance directly measures the mass collected on the exchangeable filter cartridge by monitoring the corresponding frequency change.

•Mass calibration may be verified, using an filter of known mass.

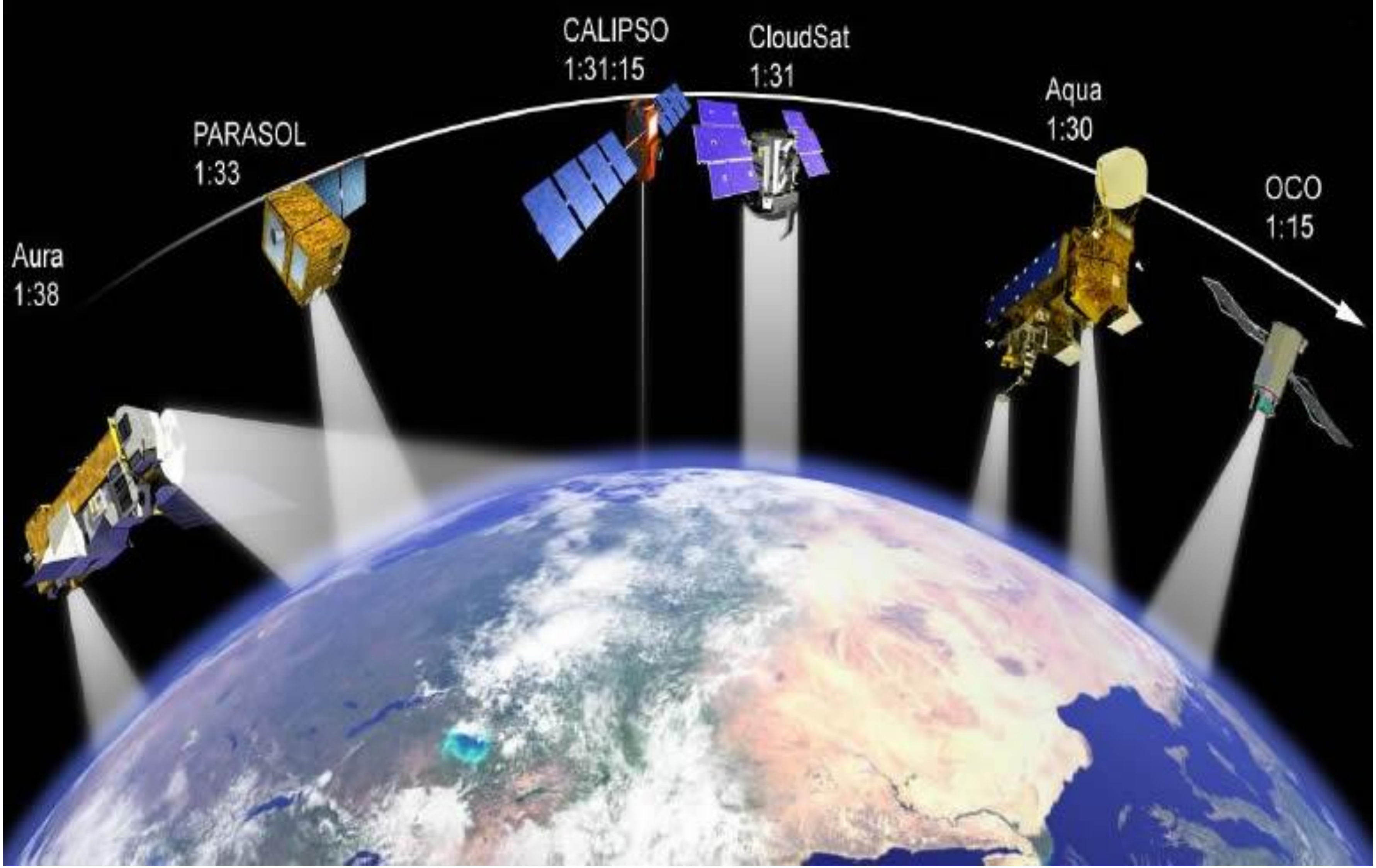
•Active flow control is maintained and set points are constantly adjusted in accordance with ambient temperature and pressure.

How many in a particular size fraction

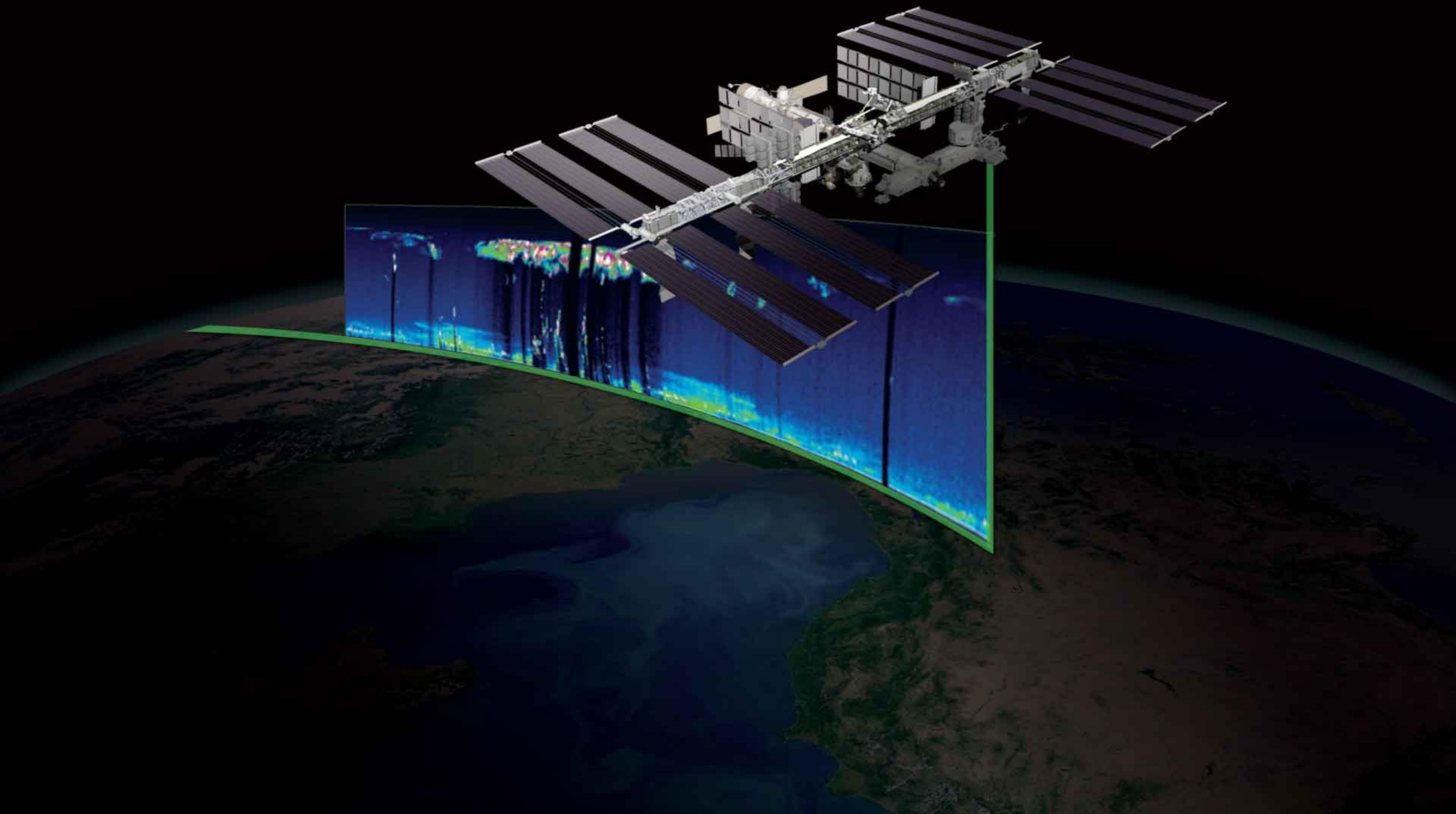


Particle size affects scattering of the light beam

Remote Sensing:
Spectroscopy from the sky



Remote Sensing: Spectroscopy from the sky

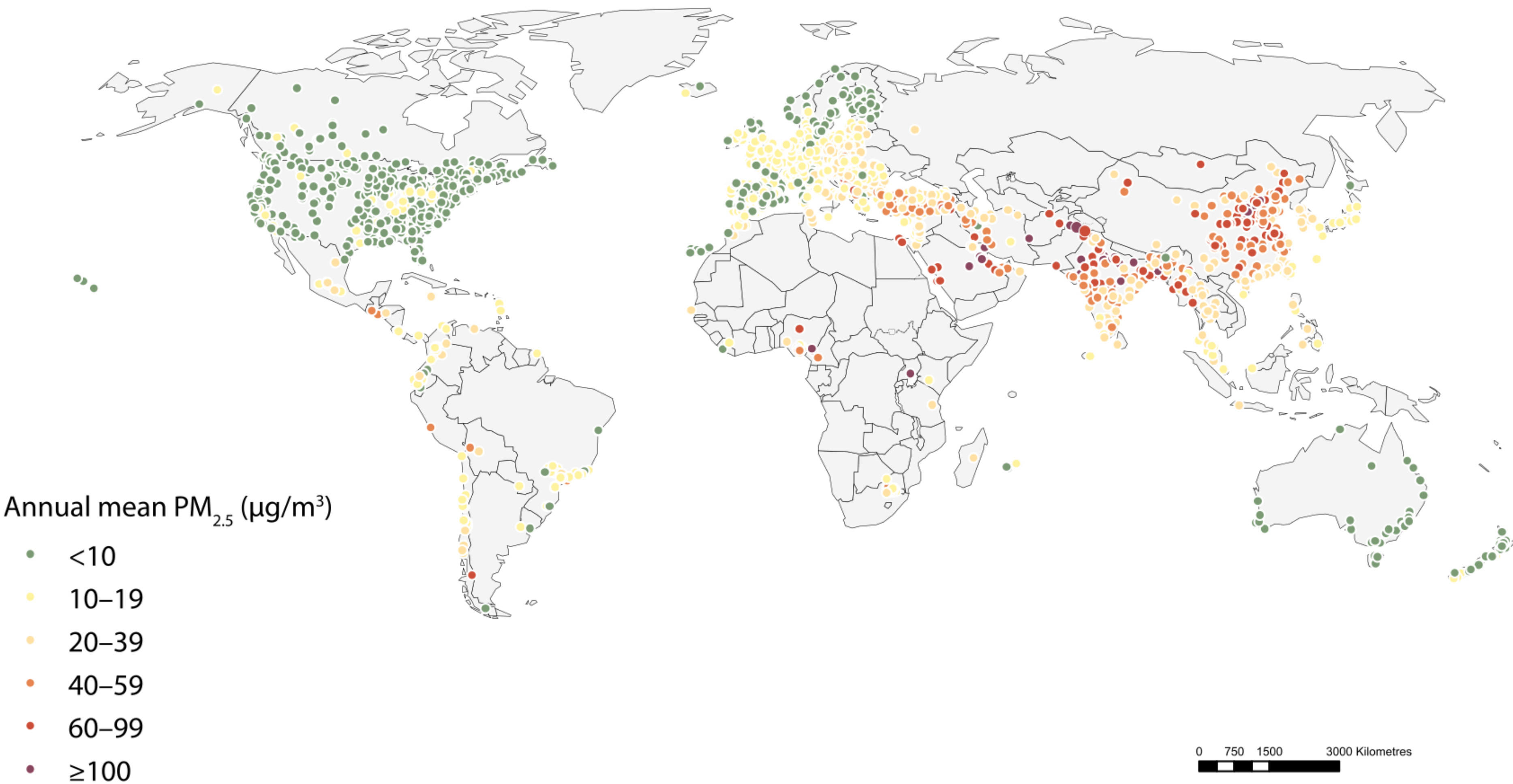


AERONET - NASA

LOW COST SENSORS (LCS)

Which world regions suffer the poorest air quality?

Figure 2: Location of the monitoring stations and $PM_{2.5}$ concentration in nearly 3 000 human settlements, 2008-2015



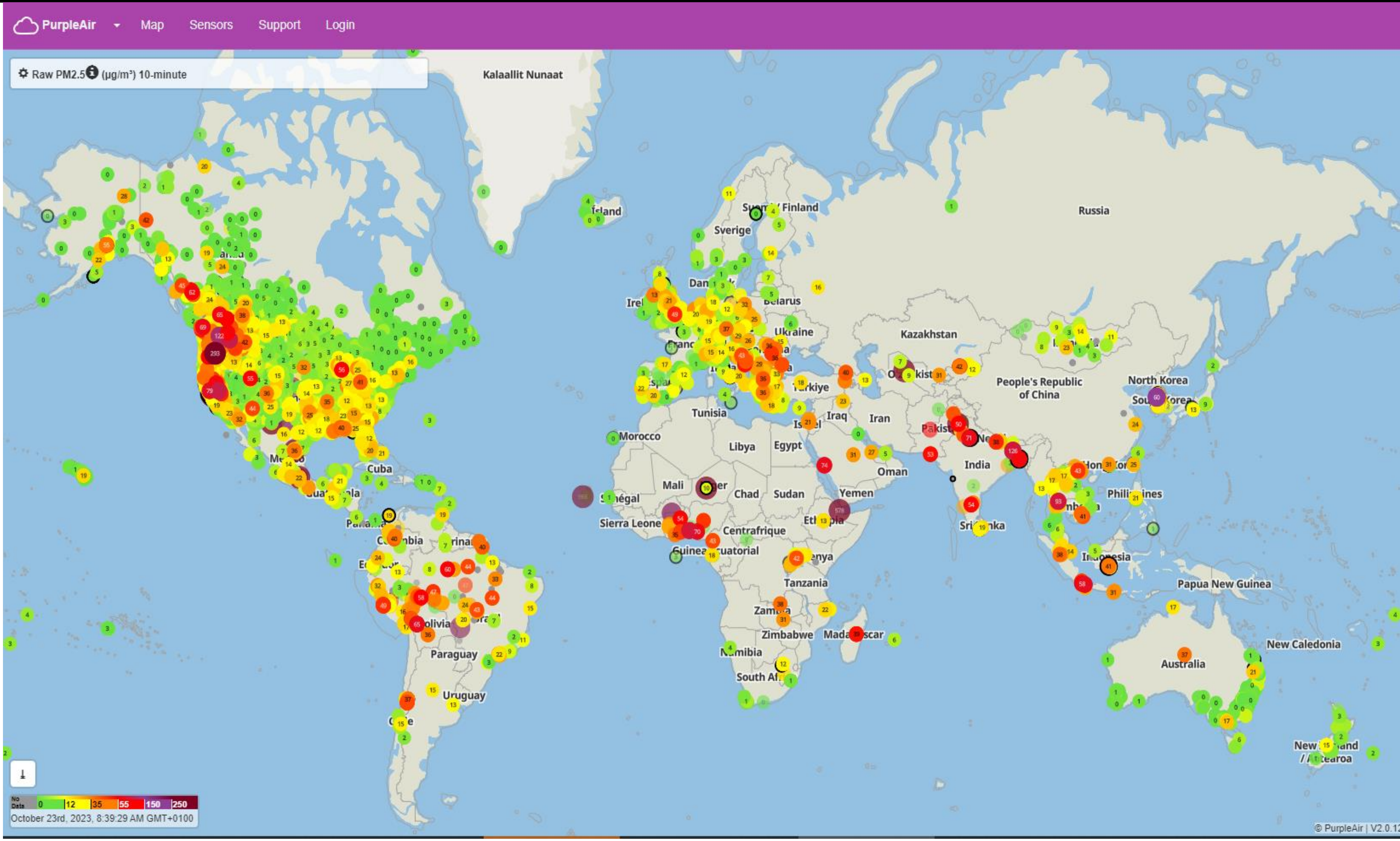
WHO, (2016)


www.purpleair.com


breathelondon.org
clarity
clarity


EARTH SENSE

Low Cost Sensor Networks



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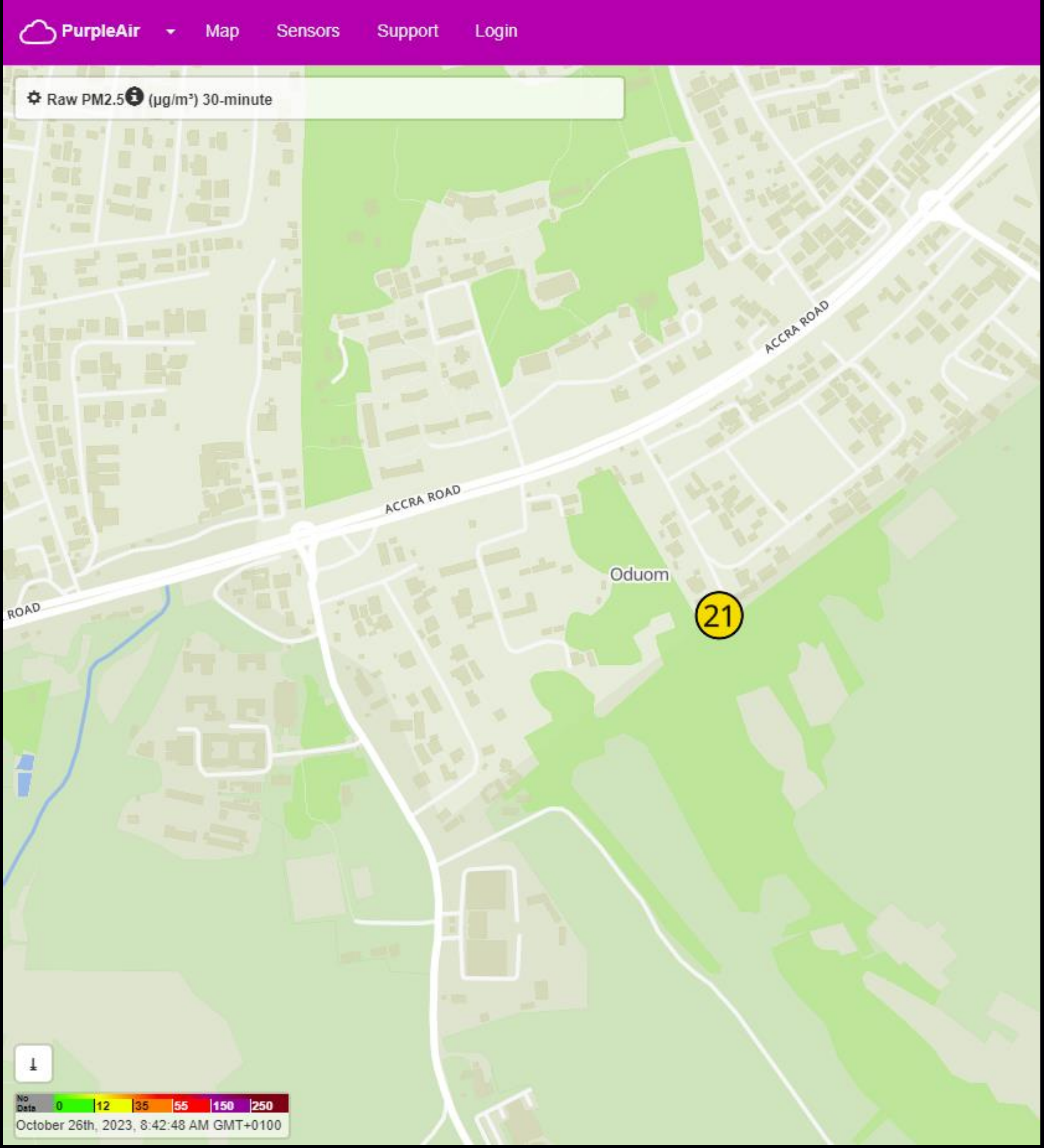
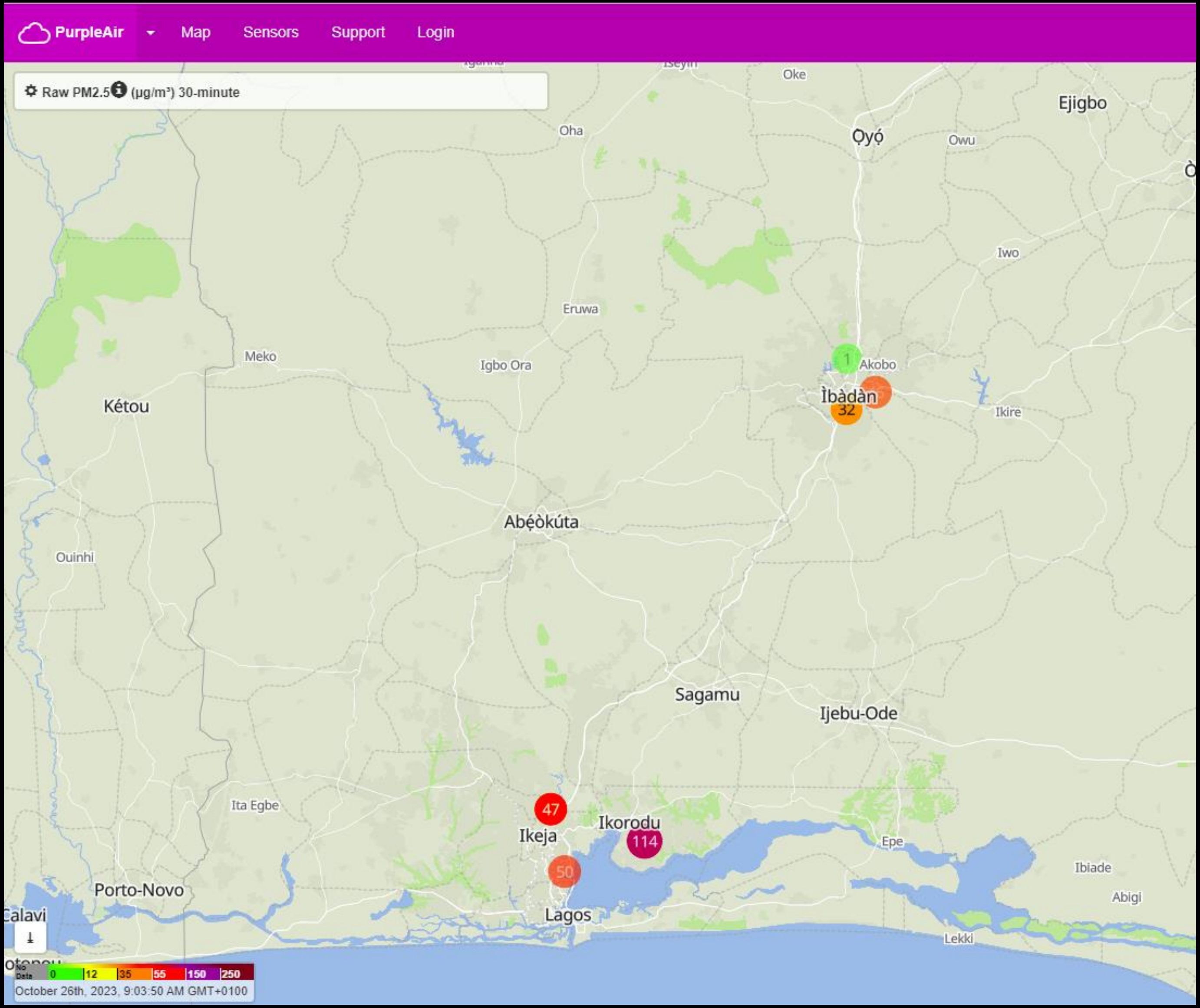
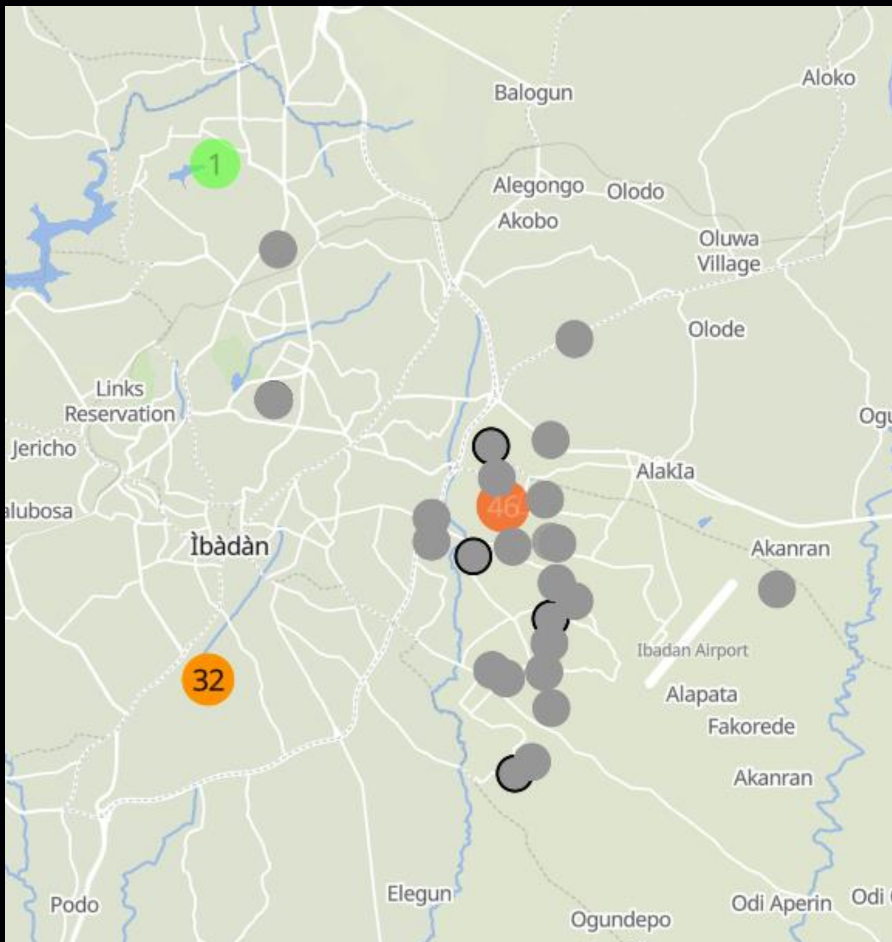
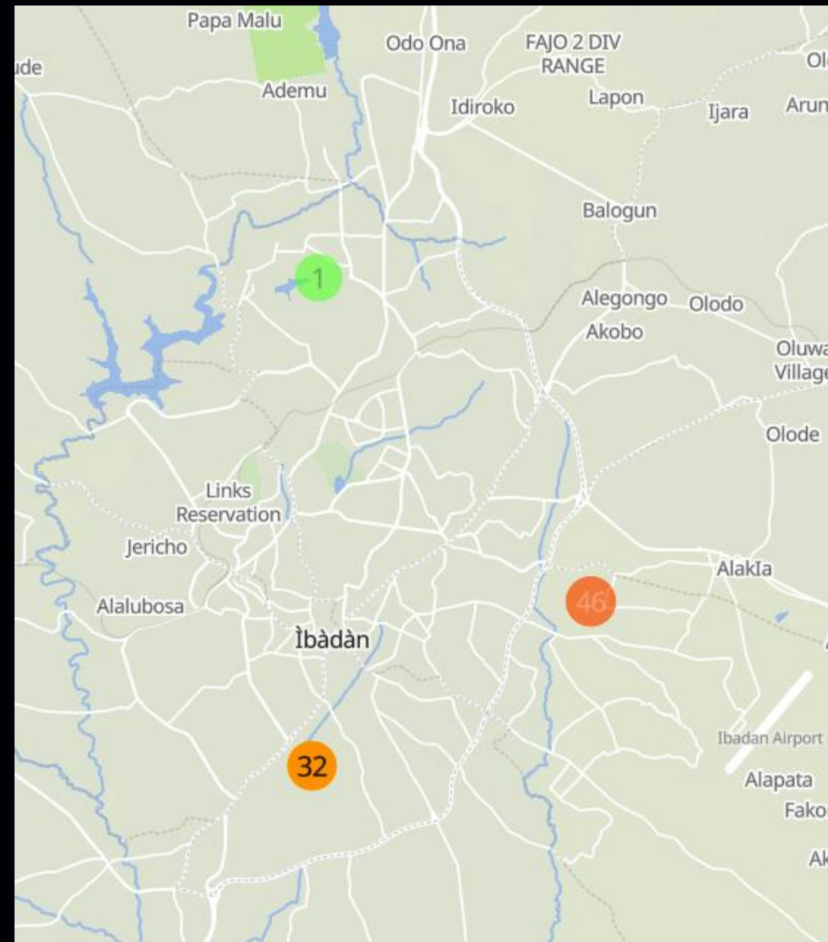

PurpleAir
Map
Sensors
Support
Login
Raw PM2.5 (µg/m³) 30-minute
ACCRA ROAD
ACCRA ROAD
ROAD
Oduom
21
No Data
0
12
35
55
150
250
October 26th, 2023, 8:42:48 AM GMT+0100

Local Networks



Local Networks





In the last year…. TODAY!

Measurements matter!